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Interactive comment on “A geochemical modelling study of the evolution of the chemical composition of seawater linked to a global glaciation: implications for life sustainability” by G. Le Hir et al.

Anonymous Referee #2

Received and published: 1 August 2007

This manuscript models the chemical evolution of the global ocean during the course of a hard Snowball glaciation and its immediate aftermath. Currently, there is a poor understanding of the geochemical consequences of a Snowball Earth glaciation. As such, this paper is a welcome contribution to the topic, providing concrete predictions for the geochemical evolution of the Snowball ocean. While there remains significant debate about the existence of a 'hard' Snowball (i.e., equatorial sea ice), its likely duration, the activity of the hydrological cycle, and the degree of ocean-atmosphere exchange, Le Hir et al. stake out a particular scenario (a 30 Myr hard snowball glaciation) and

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model the geochemical consequences under a variety of different conditions (e.g., sea floor weathering; ocean-atmosphere contact). The results presented in this text provide a series of geochemical predictions that can be tested (by Snowball proponents and critics alike) against the geochemical record as preserved primarily within the cap carbonates overlying the glacial diamictites.

The authors frame their modeling study as an attempt to investigate the apparent disparity between the geologic/geochemical evidence for dramatic environmental change and a record that suggests no significant biological changes associated with the Snowball glaciation(s) (citing Corsetti et al., 2006). However, there is ample evidence for progressive (eukaryotic) biological evolution in the aftermath of the Marinoan glaciation, particularly from the Doushantuo Formation in China (Yin et al., 2007 and references therein). Although not discussed in the text, this is consistent with the authors' modeling results that suggest that any evolutionary disturbances would likely occur in the immediate post-glacial environment, believed to be characterized by severe and rapid environmental changes (e.g., pH, oxygen availability, temperature). As such, the text would best be revised to either eliminate the background assumption of biological stasis and focus on the geochemical heart of the paper or to recast the paper in light of the evidence for post-Marinoan biological change (Yin et al., 2007).

The modeling results presented here are predicated on the assumption that there is a complete shutdown in the delivery of continental weathering products to the ocean. This is a convenient end member scenario for modeling, but is unlikely to reflect the reality of these Neoproterozoic glaciations. There is evidence for active hydrological cycle in these glacial cycles (Leather et al., 2002). Even if these observations merely reflect processes associated with ice advance and retreat at the onset or termination of glaciation (and thus not 'true' Snowball conditions), models indicate that there will be a dynamic ice cycle throughout Snowball Earth glaciation (Goodman and Pierrehumbert, 2003). Based on observations of modern sediment transport by ice movement (O Co-faigh et al., 2007), this dynamic ice cycle would assuredly deposit significant sediments

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to the ocean (Goodman and Pierrehumbert, 2003). These sediments and their weathering products are likely to alter the pH buffering capability and the alkalinity of the ocean, as well as the size and isotopic composition of the DIC reservoir. The volume of these sediments and their contribution to the evolution of ocean chemistry needs to be assessed, particularly given that a significant portion of these sediments are likely to have been derived from platformal carbonates (Goodman and Pierrehumbert, 2003).

Sea floor weathering is presented as the main mechanism to change (e.g., Ca/Mg ratio) and buffer (pH) ocean chemistry during a Snowball glaciation. One question that arises is whether, given the enhanced rates of sea floor weathering at the low pH predicted in the model (~ 6), it is possible to exhaust or diminish the weathering (buffering) capability of the sea floor. A statement to address this effect or demonstrate that the change would be minor would provide more confidence in the conclusions.

The Neoproterozoic glacial deposits contain a mix of reworked clasts and syndepositional sediments. As such, these strata contain relict geochemical signals from inherited clasts in addition to a component that may reflect syndepositional chemical conditions. It is therefore difficult to reconstruct a reliable record of chemical evolution during a Snowball glaciation. Despite this, the glacial deposits contain useful geochemical information. In particular, glacial intervals are characterized by synglacial carbonate clasts and/or sediments (Leather et al., 2002). The presence of carbonate clasts and specifically of ongoing carbonate deposition argues against the acidic pH conditions suggested here. Whether this is evidence for non-acidic pH during a Snowball or merely reflects conditions during ice advance or retreat that were not representative of the glaciation itself is not clear. However, the occurrence of these carbonates needs to be reconciled with the present modeling results.

The distinctive signatures of the cap carbonates are the primary record of geochemical changes during and immediately after the Snowball event. As such, it is essential that any model of the evolution of the Snowball ocean explain or at least be consistent with the salient features of the cap. Certainly, the model results presented here predict the

presumed oxygen deficiency necessary for the iron formations. In addition, the suggested explanation for the $\delta^{13}\text{C}$ excursion as a pH-dependent speciation effect is quite clever. However, one glaring contradiction (acknowledged by the authors) remains regarding the mineralogy of the cap carbonate. The modeled evolution of the ocean described by the authors arises predominantly from sea floor weathering and results in a calcium-rich, magnesium-depleted ocean that would be expected to precipitate calcite. However, one of the most widespread and distinctive features of cap carbonates is a basal dolostone layer, which underlies a deeper water limestone (Hoffman et al., 2007). The dolostone layer seems to record the post-glacial transgression (Hoffman et al., 2007) and thus, presumably most closely reflects the syn-Snowball ocean composition. A model of Snowball ocean evolution should be able to ideally predict (or at least be reconciled with) early post-Snowball dolomite deposition.

There are probably several ways to reconcile the present model with the observations of early dolomite precipitation. One possible suggestion is outlined below:

As Le Hir et al. note, the Snowball period is believed to deplete the ocean reservoir of sulfate (Hurtgen et al., 2006). Given that sulfate is believed in part to inhibit dolomite precipitation (Baker and Kastner, 1981), one interpretation then of the dolostone-limestone transition is that it represents the transition from a low sulfate ocean to one whose sulfate reservoir has built up to a level that inhibits dolomite formation. The fact that a barite layer is often observed at the dolostone-limestone contact (Hoffman et al., 2007) likely reflects the mixing of deep (Snowball) waters enriched in Ba^{2+} and post-glacial runoff enriched in sulfate. If the effect of decreased sulfate does more to encourage dolomite formation than the low Mg/Ca ratio does to hinder it, then the present model, while not providing an intuitive explanation for the mineralogy of the cap carbonates, would then at least not contradict it.

Whether or not this is the case, more discussion in the present paper should be devoted to reconciling the model with the observation of dolomite deposition in the basal cap carbonates.

Finally, there are several small technical corrections to the text. On p. 1846, text indicates a decrease in temperature from 20°C to 26°C. Based on later text, this is likely to be a decrease to 2°C. The text maintains that the dissolution of carbonates during the glaciation is insufficient to maintain carbonate saturation ($\omega \ll 1$); however, Figure 6 and its caption indicate that ω stabilizes at 1 throughout the glaciation. This needs to be resolved. Throughout the text, there is a tendency to state supposition that is not necessarily widely held as fact (p. 1855 "Since Neoproterozoic primary producers were cyanobacteria": algal production is likely to have been at least as important; p. 1858: "obviously, cap dolostone were accumulated through the mediation of microbial activity": the presence of variable amounts of TOC is not *prima facie* evidence for biogenicity). Overall the text could benefit from further proofing of syntax and grammar.

In summary, this manuscript provides much needed quantitative modeling of ocean chemistry during and after a Snowball Earth glaciation. While additional work should be done to address the influx of glacial-derived sediments during the Snowball and to demonstrate that the proposed chemical evolution is consistent with (or is at least not contradicted by) the observations from cap carbonates, this paper takes the community forward in its understanding of geochemical changes predicted to have occurred during a Snowball glaciation.

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4, S1045–S1050, 2007

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